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KINETICS OF HMX AND CP DECOMPOSITION AND THEIR EXTRAPOLATION FOR LIFETIME ASSESSMENT*

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ABSTRACT

Decomposition kinetics are determined for HMX (nitramine octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) and CP (2-(5-cyanotetrazolato) pentaammine cobalt (III) perchlorate) separately and together. For high levels of thermal stress, the two materials decompose faster as a mixture than individually. This effect is observed both in high-temperature thermal analysis experiments and in long-term thermal aging experiments. An Arrhenius plot of the 10% level of HMX decomposition by itself from a diverse set of experiments is linear from 120 to 260 °C, with an apparent activation energy of 165 kJ/mol. Similar but less extensive thermal analysis data for the mixture suggests a slightly lower activation energy for the mixture, and an analogous extrapolation is consistent with the amount of gas observed in the long-term detonator aging experiments, which is about 30 times greater than expected from HMX by itself for 50 months at 100 °C. Even with this acceleration, however, it would take ~10,000 years to achieve 10% decomposition at ~30 °C. Correspondingly, negligible decomposition is predicted by this kinetic model for a few decades aging at temperatures slightly above ambient. This prediction is consistent with additional sealed-tube aging experiments at 100-120 °C, which are estimated to have an effective thermal dose greater than that from decades of exposure to temperatures slightly above ambient.

INTRODUCTION

Accelerated aging tests play an important role in assessing the lifetime of manufactured products. There are two basic approaches to lifetime qualification. One tests a product to failure over range of accelerated conditions to calibrate a model, which is then used to calculate the failure time for conditions of use. A second approach is to test a component to a lifetime-equivalent dose (thermal or radiation) to see if it still functions to specification. Both methods have their advantages and limitations.

A disadvantage of the 2nd method is that one does not know how close one is to incipient failure. This limitation can be mitigated by testing to some higher level of dose as a safety margin, but having a predictive model of failure via the 1st approach provides an additional measure of confidence. Even so, proper calibration of a failure model is non-trivial, and the extrapolated failure predictions are only as good as the model and the quality of the calibration.

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This paper outlines results for predicting the potential failure point of a system involving a mixture of two energetic materials, HMX (nitramine octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) and CP (2-(5-cyanotetrazolato) pentaammine cobalt (III) perchlorate). Global chemical kinetic models for the two materials individually and as a mixture are developed and calibrated from a variety of experiments. These include traditional thermal analysis experiments run on time scales from hours to a couple days, detonator aging experiments with exposures up to 50 months, and sealed-tube aging experiments for up to 5 years.

Even though HMX and CP clearly interact with each other under severe thermal exposure conditions, the mixture is still quite stable thermally when compared to most energetic materials. Our conclusion is that sealed mixtures of HMX and CP will not have significant deterioration over a few decades at temperatures $<40^{\circ}\text{C}$.

EXPERIMENTAL AND KINETIC METHODS

HMX (Lot # 81H030-033) used in the thermal analysis experiments was manufactured by Holston Defense Corporation. CP was manufactured by Pacific Scientific of Chandler, AZ. Lot #82936 was used for the thermal analysis experiments, and Lot # 81931 was used for the sealed-tube experiments.

A Differential Scanning Calorimeter (DSC), TA Instruments Model 2920, and its associated software, Universal Analysis, were used to monitor the rate of reaction of HMX-CP mixtures. These experiments used hermetically sealed pans. Sample sizes were typically 0.45 mg, and heating rates were 0.1, 0.35, and $1.0^{\circ}\text{C}/\text{min}$.

Weight loss measurements of HMX, CP, and mixtures thereof were carried out using a TA Instruments Simultaneous Differential Thermogravimetric Analyzer (SDT), model 2960, and TA open aluminum pans. From 0.4 to 3 mg of total material was used, but never more than 1.5 mg total (HMX + CP). Degradation was carried out under nitrogen carrier gas at a flow rate of $100\text{ cm}^3/\text{min}$. Isothermal experiments were conducted between 190 to 250°C .

A group of detonators containing CP and HMX were aged isothermally in ovens at 50 , 75 , and 100°C for periods of 24 and 50 months. Three to five detonators were exposed at each condition. Two detonators were analyzed at the start for a baseline. Five detonators were held at room temperature for 50 months and used as controls. Independently, a set of sealed tubes containing only HMX were heated for up to 5 years at temperatures of 60 , 80 , 100 , and 120°C , with evolved gases analyzed at six months intervals. A subsequent set of sealed-tube experiments exposed 100 mg of HMX, 100 mg of CP, or 200 mg of a 50/50 mixture for one week and one month at temperatures of 100 and 120°C . Tubes were backfilled with 1% Ar in He at a pressure of ~ 1 atm. The evolved gases were analyzed by gas chromatography. In order to resolve water and ammonia in addition to other gases, a Haysep C column was used.

Chemical reactions are often treated mathematically as 1st-order reactions with their temperature dependence described by the Arrhenius rate law: $k=A\exp(-E/RT)$, where E is the activation energy. Even when the reaction is not 1st-order, it is generally possible to describe the temperature dependence at any specific reaction extent as an exponential function of

temperature. In the simplest form, plotting the inverse of the time for a given reaction extent versus reciprocal temperature will be a straight line with slope $-E/RT$. More generally, this method is called isoconversional kinetic analysis when E is determined as a function of reaction extent.

A reaction model we have found to be particularly adaptable to a wide range of materials is the extended Prout-Tompkins model^{1,2}

$$d\alpha/dt = k(1-q(1-\alpha))^m(1-\alpha)^n, \quad (1)$$

where α is the fraction reacted, n is the reaction order, m is a nucleation-growth parameter, and q is an initiation parameter. It has limits of the original Prout-Tompkins model ($m = n = 1$), a first-order reaction, and an n th-order reaction, which is equivalent to a gamma distribution of frequency factors.¹ This reaction model was fitted to some data sets using the LLNL kinetic analysis program Kinetics05.¹

RESULTS AND DISCUSSION

A. Long-term Aging Studies of HMX-CP Mixtures in Detonators. The fractions decomposed in these experiments can be used to calibrate a kinetic model for extrapolation to other times and temperatures. Equation (1) was used with n and q constrained to 1.00 and 0.99, respectively. The results are shown in Figure 1. The reaction is strongly acceleratory, or autocatalytic, as indicated by the m value of 1.83. This means that the reaction quickly takes off after a long period of latency (induction period).

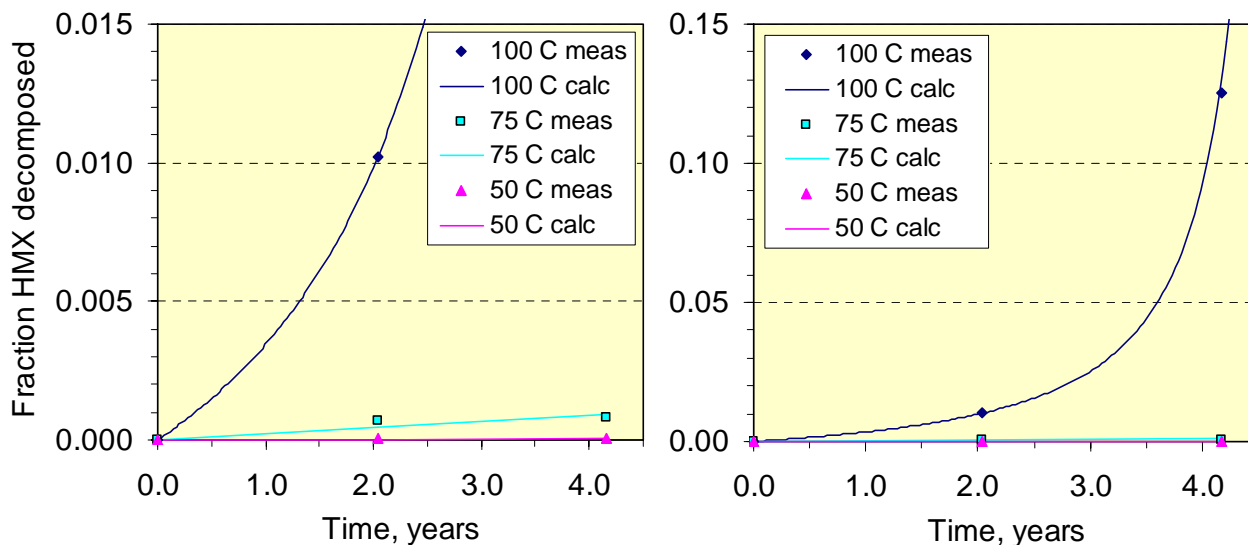


Figure 1. Observed and calculated fractions of HMX decomposed for a fit of an extended Prout-Tompkins nucleation-growth model to the Sandia detonator aging studies. The kinetic parameters are $A=8.95 \times 10^8 \text{ s}^{-1}$, $E=109.7 \text{ kJ/mol}$, $m=1.83$, $n=1.00$, and $q=0.99$. Two scales are shown for a better view of the comparison between experiment and calculation. The acceleratory nature of reaction causes it to be nearly complete by 5 years at 100 °C.

B. HMX decomposition kinetics. To assess whether the amount of gas generation from the detonator experiments is greater than expected for HMX alone, results from a variety of HMX experiments were compiled and analyzed. These results were obtained from open-pan TGA, sealed-pan DSC, and gas-generation measurements at high and low temperatures. Data was taken from the literature^{3,4} and from experiments conducted specifically for this work. The objective was to determine whether the reaction follows a single activation energy over a wide temperature range and to estimate rates of gas generation rates at the detonator aging temperatures (50-100 °C).

Kinetic analysis of isothermal TGA data from 190 to 250 °C and nonisothermal TGA and DSC data for heating rates from 0.1 to 1.0 are summarized in Table 1 and Figures 2-4. The main stage of the reaction (ignoring minor mass losses due to moisture and sources near the $\beta \rightarrow \delta$ phase transition) is well characterized by a single autocatalytic reaction, even though deviation from the model indicates the presence of multiple rate processes. The deviation from a single peak is most noticeable at the slowest DSC heating rate in Figure 4.

For the open-pan isothermal TGA experiments, a 2% weight loss occurred essentially during sample heatup, likely occurring due to loss of residual moisture. Kinetic parameters are reported for only the main stage of HMX decomposition in the ramped TGA and DSC experiments. In the TGA-DTA experiments, a weight loss process occurred just above the solid-solid phase transition, but the amount of weight loss was inversely proportional to heating rate. At high heating rates, the weight loss spikes might be associated with either a small exotherm or endotherm in the DTA and may be due to impurities. At low heating rates where the mass loss was larger, there was a larger exotherm, which may result from interaction with the purge gas (residual moisture or oxygen) during the extended heatup. It is not obvious that any of these early signals are related to HMX decomposition itself. In the DSC experiments, no early processes could be distinguished from the phase transition endotherms. Consequently, we do not have any convincing evidence in any of the three data sets that there is a HMX decomposition process other than the main reaction, i.e., the continuous and obvious process occurring, for example, between 200 and 270 °C in Figure 3.

Even though a good fit to the main reaction can be obtained with a single nucleation-growth reaction model, it must be emphasized that it is not a single homogeneous process. Inflections in reaction rate plots show clear evidence for multiple overlapping processes. Empirical models having three parallel reactions have been developed to attain a marginally better fit,³ but they have not been used in this study.

Behrens and Bulusu⁴ studied the decomposition of HMX using evolved gases as a measure of the reaction. This particular paper added data in the 175-200 °C range to earlier work from 210 to 235 °C. The reaction showed clear evidence of induction and acceleratory phases, and HMX sublimation contributed significantly to the gas formation rate in the early stages of the reaction. Individual gas species had different release kinetics, e.g., evolution of CH₂O lags that of N₂O.

Behrens and Bulusu⁴ describe their kinetics in terms of three sequential processes, which over the small reaction interval studied, are essentially straight lines. The first process is an induction period, in which gas generation occurs, and the induction time is described by an Arrhenius-like relationship. The acceleratory phase is described by two sequential first-order reactions operating over time intervals that are calculated to achieve prescribed fractions reacted.

Equation (1) automatically achieves these characteristics with a continuous function. Consequently, we reanalyzed the results of Behrens and Bulusu using our approach. The results are shown in Figure 5. The model fits the data well. The resulting A and E parameters are intermediate between Behrens' first and second acceleratory phase Arrhenius parameters. Figure 6 shows a similar comparison to the fractions reacted calculated from the main reaction of our kinetic expression calibrated on open-pan TGA data (Table 1). The agreement is very good at 200 °C and within a factor of two at 175 °C. The gas evolution data is more strongly autocatalytic, and there may be a contribution from sublimation to the TGA model.

Table 1. Summary of kinetic parameters from thermal analysis of HMX sample B-844.

	fraction	A, s⁻¹	E, kJ/mol	m	n
Isothermal TGA	0.02	7.04×10^7	101.1	0.00	1.00
(open pan, 190-250 °C)	0.98	5.84×10^{13}	167.2	0.691	0.823
Ramped TGA	1.00	1.087×10^{11}	141.4	0.539	0.483
(open pan, 0.1-1.0 °C/min)	see text				
Ramped DSC	1.00	3.81×10^{13}	164.4	0.635	0.320
(hermetically sealed pan)	see text				

Another source of HMX decomposition data comes from multi-year, low-temperature, sealed-tube experiments at Sandia-NM. N₂O generation over 5 years for temperatures ranging from 60 to 120 °C are shown in Figure 7. For example, these experiments achieved 5% HMX decomposition in 2.7 years at 120 °C, based on the conversion of HMX nitrogen to N₂O, which is the only gas reported. By analogy to the aging experiments summarized in Table 1, we estimate that the fraction reacted as measured by mass loss of HMX would be only half as great as that estimated from nitrogen conversion. Similarly, the maximum yield at 100 °C (as measured by N₂O generation) was 1% from 1.5 to 3.5 years. These and additional 80 °C experiments result in a low apparent activation energy of 96 kJ/mol. However, the flatness in 100 °C gas yield from 1.5 to 3.5 years is reminiscent of a faster process for the first percent or so of decomposition in thermal analysis experiments and may not be representative of the bulk reaction.

A requirement for kinetic analysis is that unless the reaction is demonstrated to follow an assumed model exactly, one must use comparable extents of reactions at all measurement temperatures for the A and E determination or they can be distorted by the characteristics of the model assumed—either higher or lower than the true values. Consequently, kinetics parameters calibrated on this low conversion data are not particularly reliable. Instead, we view this data, particularly the rate at 120 °C, as an excellent way to test the extrapolation of the more extensive work at higher temperatures to the conditions of interest for the accelerated aging tests.

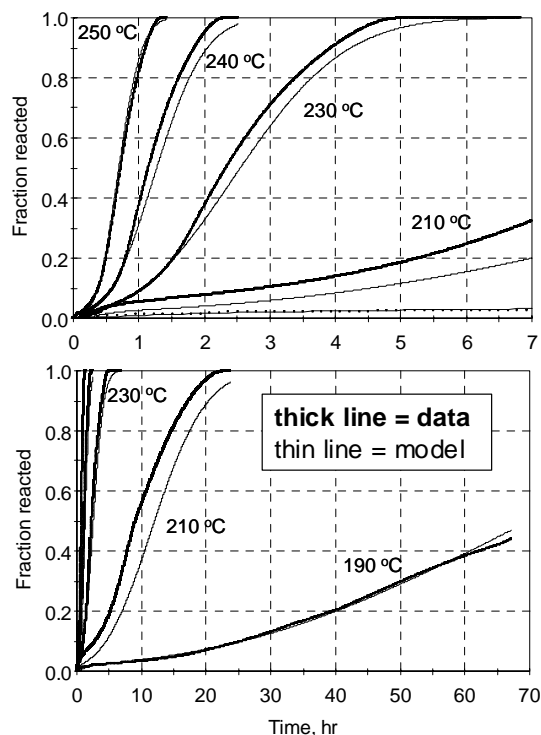


Figure 2. Comparison of model parameters in Table 2 for isothermal weight loss from HMX (open-pan TGA). Two time scales are shown enable a comparison over the entire temperature range. Only partial reaction was achieved at 190 °C due to the slowness of the reaction. The autocatalytic character ($m > 0$) is particularly evident at the lower temperatures where it is clearly separated from thermal heatup.

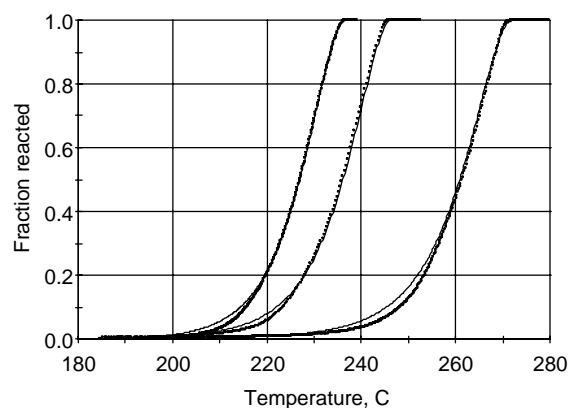


Figure 3. Comparison of model and experiment for weight loss (open-pan TGA) at heating rates of 0.1, 0.2, and 1.0 °C/min, from left to right, respectively. The thin line is the model.

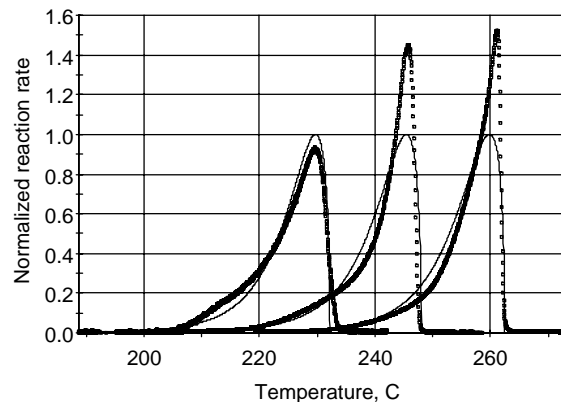


Figure 4. Comparison of model (lines) and experiment (points) for DSC heat release in a hermetically sealed pan at heating rates of 0.1, 0.35, and 1.0 °C/min.

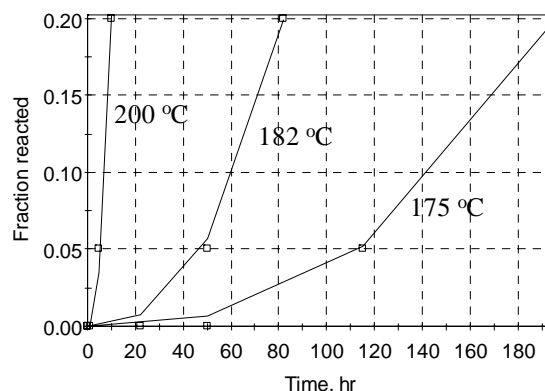


Figure 5. Extended Prout-Tompkins autocatalytic model for the low temperature HMX decomposition data of Behrens and Bulusu⁴ using $q=0.9999$. The resulting kinetic parameters were $A=7.71 \times 10^{18} \text{ s}^{-1}$, $E=210.1 \text{ kJ/mol}$, and $m=0.676$.

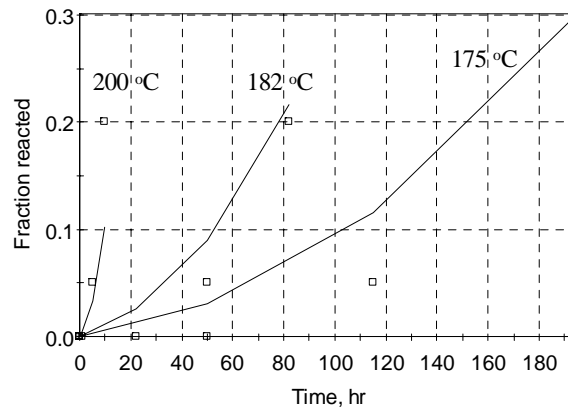


Figure 6. Comparison of HMX reacted from gas evolution data⁴ with that calculated from isothermal TGA kinetics (Table 1).

Are these various kinetic expressions consistent with the accelerated aging test data and therefore are a reliable estimator of storage lifetime of components containing HMX? Figure 8 compares the time to achieve 10% HMX decomposition for various kinetic experiments and models, which would certainly raise concern about HMX performance in a component. The various experiments actually agree very well and imply an overall activation energy of about 165 kJ/mol for the first 10% of the reaction from 120 to 270 °C. The reaction time at the lower temperature (100 °C) time of the sealed-tube experiments falls above the trend line from the other experiments, but it is not as reliable due to the extremely low extent of reaction. The 80 °C result from Figure 7 would continue that trend line, but it is an even less reliable basis to estimate a time for 10% conversion due to the very low extent of reaction.

The gas yields from the detonator aging tests are clearly greater than for HMX decomposition alone by a factor of about 30, since all the results from disparate experiments follow the same basic trend line from 270 °C down to at least 120 °C. Even though the 100 °C data point for HMX alone indicates nearly a tenfold enhancement in HMX decomposition in the CP-HMX detonator. Additional information supporting an enhanced HMX decomposition in the detonator aging tests is given in the following section, which explores the decomposition of HMX-CP mixtures.

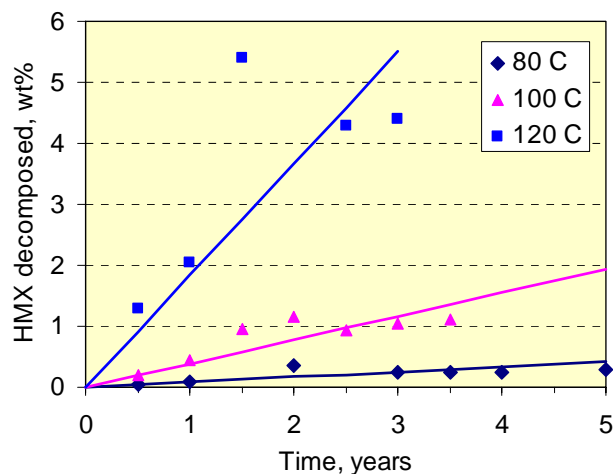


Figure 7. N₂O gas yields as a function of time from long-term HMX decomposition experiments. Based on an analogy to the more complete product analysis in Table 1, the amount of mass loss from HMX would be only half as great.

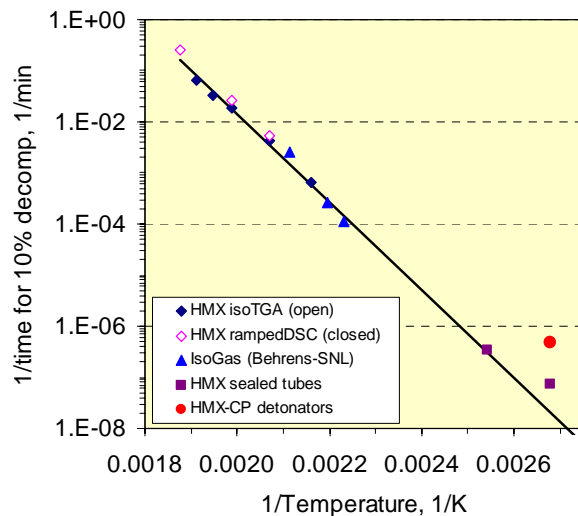


Figure 8. Compilation of rate constants for HMX decomposition from a variety of experiments. Rate constants are expressed in terms of the reciprocal time needed for 10% decomposition. The filled squares for the sealed-tube experiments represent a most likely value based on estimated mass loss.

C. High-Temperature Decomposition of CP and CP-HMX mixtures. The enhanced decomposition of HMX in the detonator accelerated aging experiments over that expected for HMX alone suggests that CP and HMX are interacting with each other. Consequently, a series of DSC experiments were performed with CP by itself and CP mixed with HMX. The

experiments used hermetically sealed pans, and the reaction rate was monitored by heat flow. The working hypothesis was that trace gases evolved from the early stages of CP decomposition accelerate the decomposition of HMX. There was some variability in the measured reaction rates, so the most representative runs from at least three replicates was used in this analysis.

Examples of the heat release for CP by itself at three different heating rates are shown in Figure 9. These reaction profiles are similar to those reported by Massis et al. for a sealed pan.⁵ Due to variability of the reaction profiles, no detailed kinetic analysis was attempted. However, analysis of the shift in T_{\max} of the sharp exotherm, using Kissinger's method,⁶ yielded an activation energy of 196.9 kJ/mol. Searcy and Shanahan⁷ report that the decomposition occurs in three stages. Stage I is an endothermic process that includes the dissociation of ammonia ligands from the cobalt atom, rearrangement of the 5-cyanotetrazolato ligand, and oxidation of the cobalt

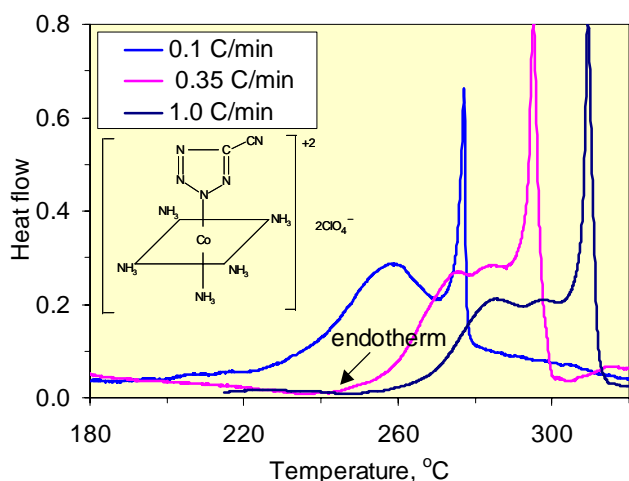


Figure 9. Reaction profiles for decomposition of CP by itself. The first stage of decomposition gives the endotherm most evident for 0.35 °C/min at 240 °C.

to the +2 oxidation state. Stage II is the oxidation of the ligands around the cobalt atom by the perchlorate ion, and Stage III is the oxidation of the residual solid products by the perchlorate ion. Because the decomposition in an open system occurs faster, more or less at the temperature of the endotherm in a closed system, it has been postulated that ammonia inhibits the exothermic decomposition.⁵ However, the endotherm itself appears to be accelerated by ammonia.⁸ Regardless of the details of the complete decomposition mechanism, it is possible that the ammonia liberated during the early, endothermic stage of CP might react with HMX to accelerate exothermic decomposition reactions for HMX.

To investigate possible acceleration of HMX decomposition by early CP gaseous products, CP and HMX mixtures were heated at both a constant temperature and heating rates. Both show clear evidence for acceleration of HMX decomposition by CP.

Results for ramped heating in hermetically sealed DSC pans are shown in Figure 10. The primary exotherm of the mixture is clearly ~20 °C lower than HMX, whose exotherm precedes that of CP by a similar amount. The 20 °C shift in the reaction profile of the mixture compared to neat HMX corresponds to an increase in the reaction rate by a factor of 6. The very beginning of the endotherm for CP alone, particularly evident at a heating rate of 0.35 °C/min, is similar to the beginning of the exotherm of the mixture. The peak of the neat CP endotherm corresponds to the early stages of HMX decomposition by itself. These simple observations provide support for the hypothesis that ammonia released from CP enhances the decomposition of HMX.

Due to the complexity of the reaction profile of the mixture in Figure 10, no comprehensive kinetic analysis was attempted. However, the first exothermic peak in the HMX-CP mixture is described fairly well by a nucleation-growth model having parameters of $A=2.22\times 10^{13}$, $E=154.8$ kJ/mol, and m and $n \approx 1$. Even though this activation energy appears to be lower than the mean value of 165 kJ/mol for neat HMX, we cannot be sure due to the variability in replicate runs.

Results for the isothermal TGA experiments for CP, HMX, and the CP-HMX are shown in Figure 11. Again, the weight loss of the mixture is clearly that the two materials independently, even though these experiments were conducted in open pans. A quantitative measure of the acceleration is difficult due to changes in character from experiment to experiment of the initial weight loss from neat CP, but generally speaking, the decomposition of the mixture is 3-5 times faster than either HMX alone or a weighted average of the two materials independently. This result is qualitatively consistent with the nonisothermal DSC experiments in Figure 10.

The acceleration appears to be greater at the lowest temperature, which supports the concept that the activation energy for decomposition of the mixture is lower than that for HMX alone. Perhaps significant is that Pickard et al.⁸ report an activation energy of 147.3 kJ/mol for the endothermic decomposition stage of CP, which is strikingly close to our estimated value for the CP-HMX mixture.

The kinetic results for the CP-HMX mixtures are shown with earlier results for HMX alone in Figure 12. The limited number of kinetic experiments and the variability in the results prevent a quantitative prediction of the mixture reactivity at 100 °C and below, but one can make a qualitative prediction. First-order kinetic parameters for HMX consistent with the various experiments are $A=2\times 10^{13}$ s⁻¹ and $E=165$ kJ/mol. If we assume that the correct activation energy for the mixture is 147 kJ/mol, the corresponding frequency factor must be 1.2×10^{13} s⁻¹ to have a 6-fold faster rate constant at 200 °C. When these two rate expressions are extrapolated to 100 °C, one finds that the rate constant for the mixture is 20 times faster than for HMX alone. Consequently, we can conclude that the combination of the faster rate for the CP-HMX mixtures at high temperatures and a lower activation energy result in an extrapolated reactivity that is qualitatively consistent with the enhanced gas generation observed in the Sandia detonator accelerated aging tests.

D. Short-term Aging Studies of HMX, CP and HMX-CP Mixtures. Because of the HMX-CP interactions found for relatively severe thermal exposures in the thermal analysis experiments, additional sealed-tube experiments were conducted for 1 week and 1 month at 100 and 120 °C. In all cases, the estimated amount of HMX decomposition is less than 0.1%. The amount of HMX decomposition may be as much as two times larger than with HMX alone, but it certainly is not substantially different. The amount of HMX decomposed individually is qualitatively as expected. A simple linear extrapolation of Figure 10 (dividing by two to obtain mass loss) predicts ~0.08% mass loss for one month and 0.02% for one week at 120 °C, in excellent agreement with these experiments. Similarly, a linear extrapolation of Figure 10

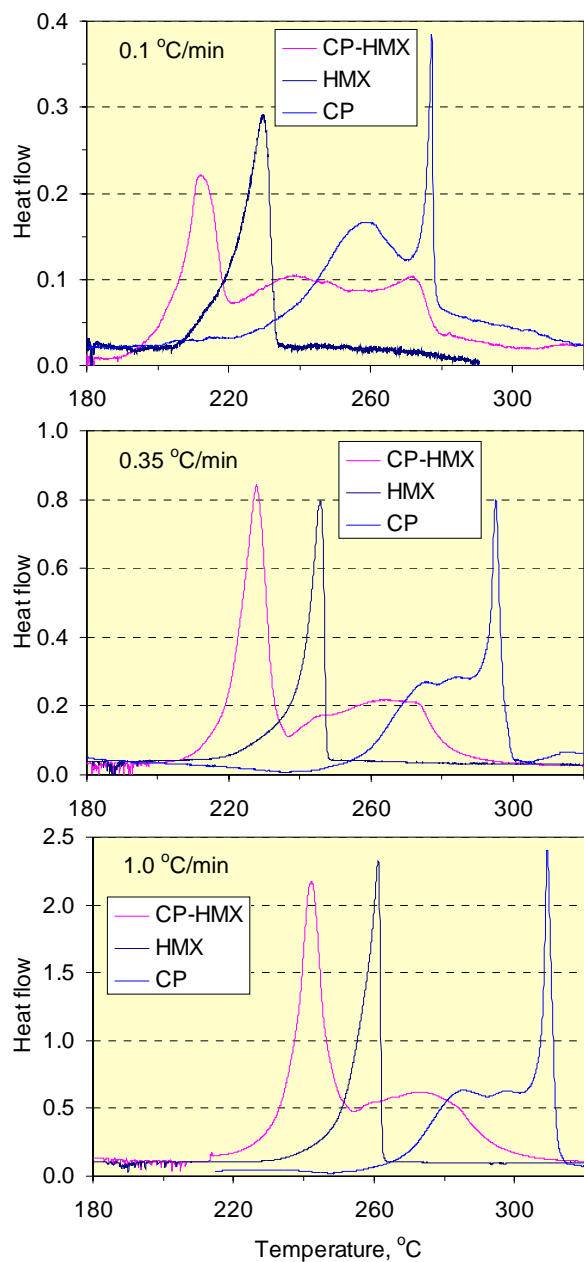


Figure 10. Comparison of DSC reaction profiles of HMX, CP, and CP-HMX mixtures. Note that the endothermic reaction for CP is coincident with the exothermic decomposition of HMX, and it is particularly evident in the profiles at 0.35 °C/min. Even though the CP-HMX mixture decomposes faster than either individually, one should compare the mixture T_{\max} of 240 °C at 1 °C/min to the corresponding values of 180 °C for PETN, 215 °C for RDX, and 275 °C for TNT.

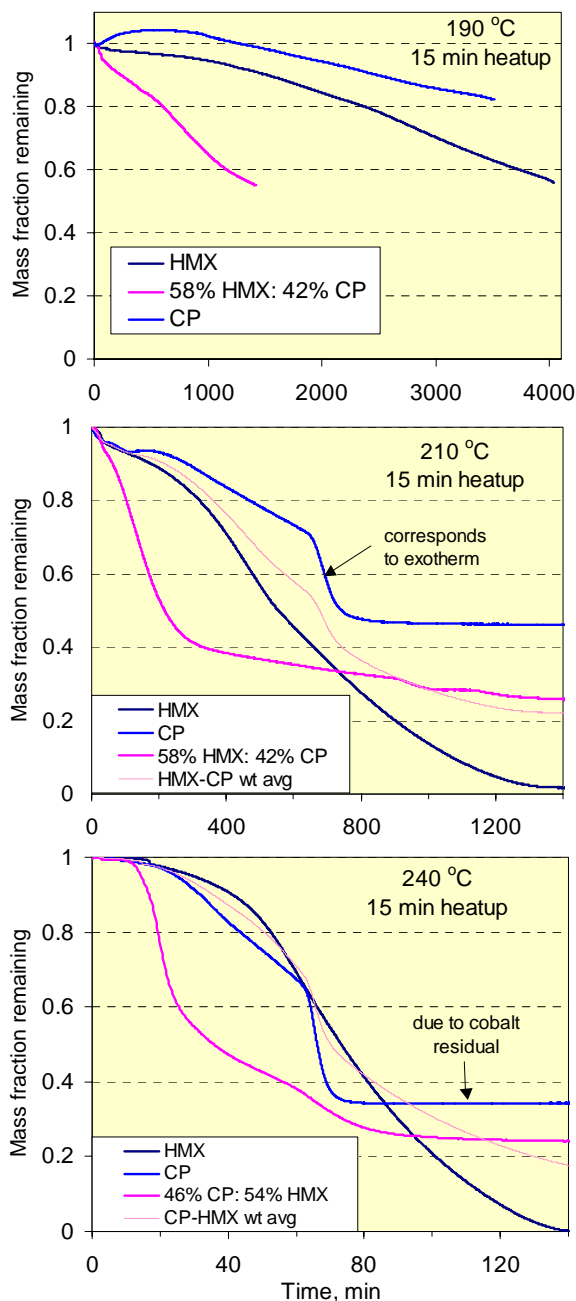


Figure 11. Comparison of isothermal weight loss for neat HMX and CP and mixtures of the two materials. The time for 10% weight loss is accelerated 3-5 times compared to either HMX alone or a weighted average of the two materials independently. The sharp mass loss for corresponds to a sharp exotherm in the simultaneous ΔT signal in the SDT apparatus and probably corresponds to rapid oxidation by perchlorate.

results predicts 0.02% decomposed for one month at 100 °C, again in excellent agreement with these short-term aging studies. The decomposition enhancement of less than two times for HMX-CP mixtures in these experiments might be due to being too early in the autocatalytic interaction. Although both HMX and CP decomposition by themselves are autocatalytic, the detonator results are more strongly autocatalytic than HMX by itself. Consequently, there may be insufficient CP decomposition products at this early stage to have had an acceleratory effect to the extent observed in detonators heated for 50 months at 100 °C.

E. Lifetime Predictions for Storage Conditions. Storage temperatures for explosives would typically be less than 40 °C, and the desired lifetime of the component would be a few decades. The allowable amount of degradation would depend on application, but it is likely in the 1 to 10% range. Figures 12 and 13 strongly support the validity of an Arrhenius extrapolation.

Although the precise lifetime may be difficult to predict, one can establish bounds by approaching the issue from different directions. First, we extend the Arrhenius plot previously shown in Figure 12 to estimate how much time would be required for 1 to 10% decomposition of the HMX. This extrapolation is shown in Figure 13. We can estimate the time for the lifetime-equivalent thermal dose in accelerated aging experiment using these activation energies and compare conclusions to the failure extrapolation approach.

The extrapolation based on a combination of the high temperature thermal analysis experiments and the gas yields from the accelerated aging tests predict that >100,000 years are needed to attain 10% HMX decomposition at 30 °C. The extrapolation based on kinetics derived solely from the accelerated aging tests is less favorable due to the lower apparent activation energy. Even so, the mixtures would be expected to survive for ~10,000 years based on this extrapolation. The equivalent-lifetime thermal-dose approach comes down clearly on the side that the lifetime of HMX-CP mixtures is much greater than required. Using a conservative value of 150 kJ/mol for E , one finds that 2 days at 100 °C and less than one hour at 120 °C are equivalent to 50 years at 40 °C. Equivalent times for 30 years at 30 °C are 10 times less.

CONCLUSIONS

HMX shows enhanced decomposition in the presence of CP in both high-temperature thermal-analysis experiments and lower temperature detonator experiments. Even so, kinetic extrapolations to a hypothetical storage temperature of 30 °C indicates that such mixtures would still last for thousands of years. Although the amount of HMX decomposition that is acceptable depends on application, it is reasonable to use a degradation value between 1 and 10% in a first-cut assessment. The predicted time for 10% decomposition is calculated to be from 10,000 to 100,000 years, based on models calibrated on detonator aging tests alone and a combination of the sealed-tube aging and thermal analysis tests. The activation energy from the latter is probably more reliable, giving the longer lifetime prediction.

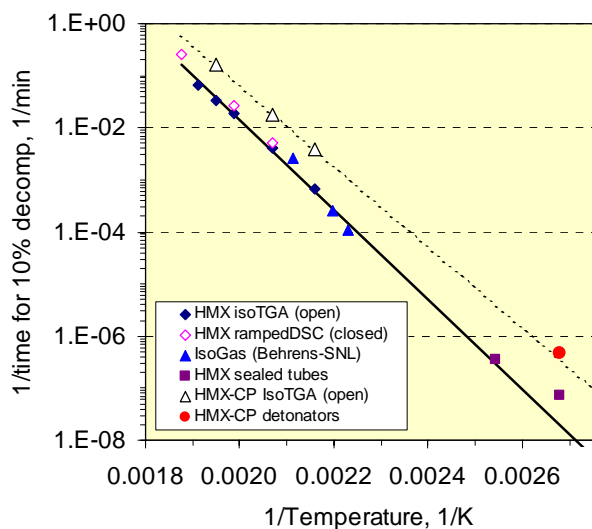


Figure 12. Arrhenius plots for HMX alone, HMX-CP mixtures, and the Sandia aging tests. The enhanced gas yields from the accelerated aging tests are qualitatively consistent with an extrapolation of the high-temperature thermal analysis experiments of CP-HMX mixtures.

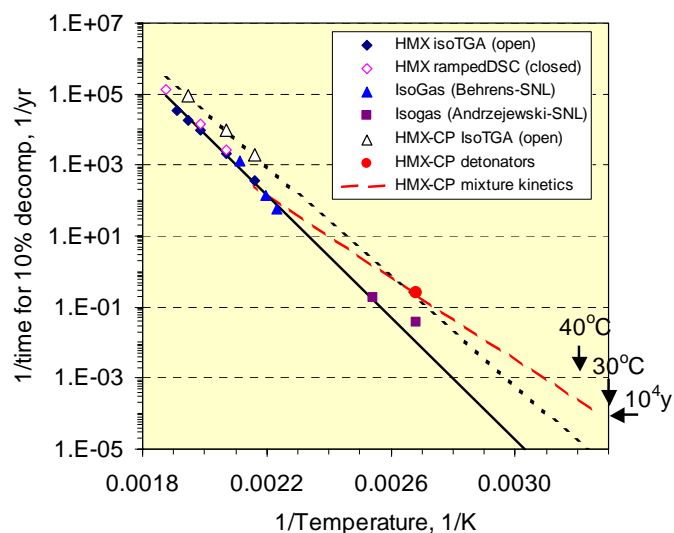


Figure 13. Prediction of mixture lifetimes at 30-40 °C based on an Arrhenius extrapolation of high-temperature and accelerated aging tests. The predicted lifetimes are much greater than required.

These long lifetimes must be qualified by the possibility that a low activation energy process related to oxidation or hydrolysis could cause a curvature of the Arrhenius relationship, even though there is substantial evidence in the literature that Arrhenius relationships can persist for >10 orders of magnitude differences in reaction rates. However, sealed-tube tests at 120 °C for a month, which actually represents an overtest of the material by several orders of magnitude, do not show any evidence of substantial reaction. This time is long enough that internal diffusion limitations should be negligible, and enhanced importance of oxidation or hydrolysis reactions could only occur if there were a continuous supply to replace depletion by reaction. Consequently, we consider this mechanistic possibility remote.

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